JET-COOLED LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF T-BUTOXY

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The vibrational structures of the $\tilde{A}^2A_1$ and $\tilde{X}^2E$ states of t-butoxy were obtained in jet-cooled laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectroscopic measurements. The observed transitions are assigned based on vibrational frequencies calculated using Complete Active Space Self-Consistent Field (CASSCF) method and the predicted Franck-Condon factors. The spin-orbit (SO) splitting was measured to be 35(5) cm^{-1} for the lowest vibrational level of the ground ($\tilde{X}^2E$) state and increases with increasing vibrational quantum number of the CO stretch mode. Vibronic analysis of the DF spectra suggests that Jahn-Teller (JT)-active modes of the ground-state t-butoxy radical are similar to those of methoxy and would be the same if methyl groups were replaced by hydrogen atoms. Coupled-cluster calculations show that electron delocalization, introduced by the substitution of hydrogens with methyl groups, reduces the electronic contribution of the SO splittings by only around ten percent, and a calculation on the vibronic levels based on quasidiabatic model Hamiltonian clearly attributes the relatively small SO splitting of the $\tilde{X}^2E$ state of t-butoxy mainly to stronger reduction of orbital angular momentum by the JT-active modes when compared to methoxy. The rotational and fine structure of the LIF transition to the first CO stretch overtone level of the $\tilde{A}^2A_1$ state has been simulated using a spectroscopic model first proposed for methoxy, yielding an accurate determination of the rotational constants of both $\tilde{A}$ and $\tilde{X}$ states.

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